

Self-discharge phenomenon of a high voltage Li(MnNi)O spinel investigated by Raman spectroscopy

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Raman spectroscopy is a very appropriate tool to enrich the knowledge of the structure of Li intercalation compounds on the atomic level [1]. Indeed, we have previously shown that a wealth of structural information including symmetry changes, local disorder, changes in bond lengths, emergence of side phases, etc... can be extracted from the Raman study of various oxide-based systems (e.g. V_2O_5 , TiO_2 , $LiCoO_2$...), providing therefore a better insight into the mechanisms governing the electrode performances [2-4].

High voltage Li(MnNi)O spinel oxides are known to be promising positive electrodes for Li-ion batteries [5,6]. We have recently reported new data on the local structural changes induced in high voltage electrode materials such as $LiMn_2O_4$ and $LiNi_{0.4}Mn_{1.6}O_4$ during the lithium insertion-extraction reactions [7]. In particular, the intermediate phases involved in both systems in a 3 phase structural mechanism have been evidenced through a rigorous Raman study of electrochemically deintercalated-intercalated samples. Furthermore, whereas XRD patterns are little affected, we have shown the great sensitivity of the Raman probe to monitor the changes in the Ni redox state in $LiNi_{0.4}Mn_{1.6}O_4$ from Ni^{2+} to Ni^{4+} during the charge-discharge processes (figure 1), which makes this technique a powerful tool to evaluate the state of charge of this cathode material. This is the first successful application of Raman microspectrometry to characterize redox species in an electrode material.

We present here a novel application of Raman spectroscopy devoted to the study of the self discharge phenomenon of LNMO. A detailed analysis of the Raman spectra based on appropriate decompositions of the spectral profiles of $Li_{1-x}Ni_{0.4}Mn_{1.6}O_4$ electrodes versus time storage in $LiPF_6/EC/DMC$ electrolyte has allowed to depict quantitatively the mechanism involved at high voltage when the electrode material is kept at rest in the charged state (figure 2). The kinetics of the self-discharge phenomenon of LNMO electrode can then be estimated. Our Raman study confirms the reversible character of the self-discharge phenomenon of LNMO electrode.

References

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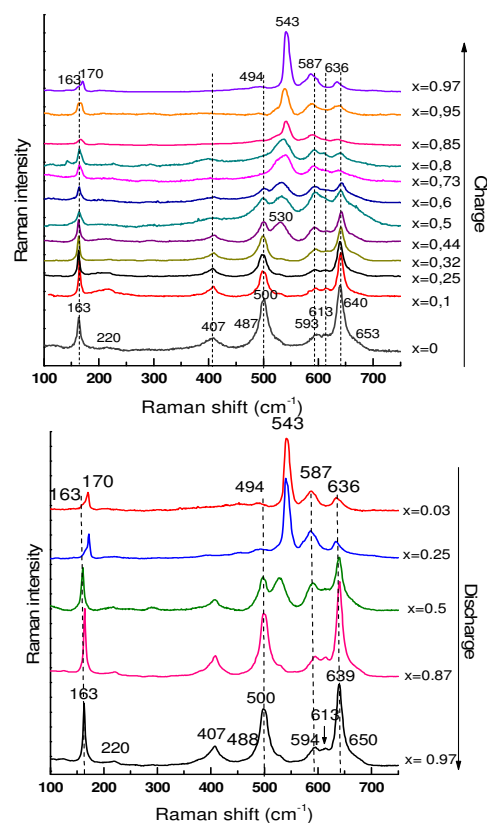


Fig. 1. Raman spectra obtained during the charge and the discharge process of a $Li_{1-x}Ni_{0.4}Mn_{1.6}O_4$ electrode

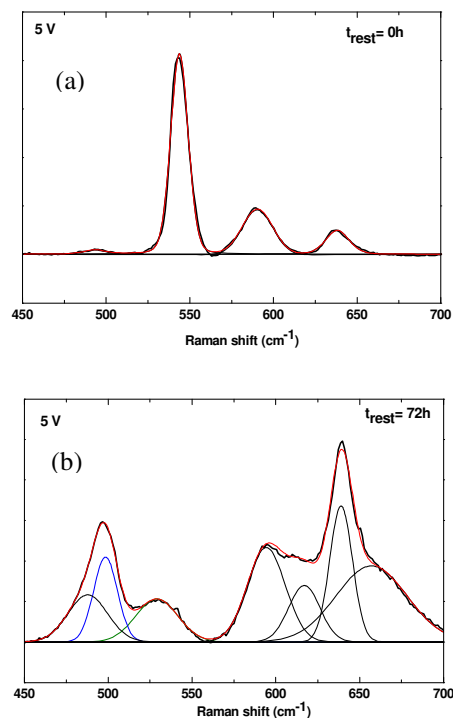


Fig. 2. Raman spectra of a $LiNi_{0.4}Mn_{1.6}O_4$ electrode charged at 5V (a) and after 72 h rest in the charged state (b)